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Mössbauer Spectroscopic Studies of the Passivation of Cobalt

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List of Manuscripts Submitted or Published under ARO Sponsorship
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- (1) "The Oxidation of Iron as Studied by Conversion Electron Mössbauer Spectroscopy," G. W. Simmons, E. Kellerman, and H. Leidheiser, Jr., *Corrosion* 29, 227-233 (1973).
- (2) "The Application of Mössbauer Spectroscopy to the Study of Corrosion," H. Leidheiser, Jr., G. W. Simmons, and E. Kellerman, *Croatica Chemica Acta* 45, 257-273 (1973).

The same paper was published in hardback edition: "Chemistry of Interfaces, Proceedings of the International Conference 1972," B. Tezak and V. Pravdic, Editors.
- (3) "Nondestructive Monitoring by Mössbauer Spectroscopy of the Rate of Corrosion of Coated Metal at the Metal-Polymer Interface," Henry Leidheiser, Jr., G. W. Simmons, and Elsie Kellerman, *Journal of the Electrochemical Society* 120, 1516-8 (1973).
- (4) "Applications of Mössbauer Spectroscopy to Corrosion and Interfacial Reactions," Gary W. Simmons and Henry Leidheiser, Jr., Chapter 3, Volume 1, "Applications of Mössbauer Spectroscopy," R. L. Cohen, Editor, Academic Press, in press.
- (5) "In Situ Mössbauer Studies of the Passive Film on Cobalt," Gary W. Simmons, Elsie Kellerman, and Henry Leidheiser, Jr., Proceedings of the Japanese-U.S.A. Collaborative Meeting on Passivity, Honolulu, March 1975, R. W. Staehle, Editor, National Association of Corrosion Engineers, in press.
- (6) "In Situ Studies of the Passivation and Anodic Oxidation of Cobalt by Emission Mössbauer Spectroscopy. I. Theoretical Background and Experimental Methods," Gary W. Simmons, Elsie Kellerman, and Henry Leidheiser, Jr., in preparation. To be submitted to *Journal of the Electrochemical Society*.
- (7) "In Situ Studies of the Passivation and Anodic Oxidation of Cobalt by Emission Mössbauer Spectroscopy. II. Spectra of Cobalt Oxides, Hydroxides, and Oxyhydroxides," G. W. Simmons, E. Samuel, and Henry Leidheiser, Jr., in preparation. To be submitted to *Journal of the Electrochemical Society*.
- (8) "In Situ Studies of the Passivation and Anodic Oxidation of Cobalt by Emission Mössbauer Spectroscopy. III. Interpretation of Spectra from Cobalt Surfaces Obtained during Anodic and Cathodic Polarization," G. W. Simmons, Elsie Kellerman, and Henry Leidheiser, Jr., in preparation. To be submitted to *Journal of the Electrochemical Society*.

Scientific Personnel Supported by this Project and Degrees Awarded
During the Period of the Grant

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Elsie Kellerman, Post-Doctorate
Eric Samuel, Post Doctorate

Emission Mössbauer spectroscopy was used to study, in situ, the chemical changes occurring at the surface of cobalt during cathodic and anodic polarization in buffered borate, pH 8.5, electrolyte. Surface sensitivity was obtained by electroplating a thin layer ($\sim 50 \text{ \AA}$) of Co doped with Co^{57} onto a cobalt substrate. Co^{57} undergoes electron capture decay that produces an excited Fe^{57} nucleus which in turn decays to the Fe^{57} ground state by gamma ray emission. Mössbauer spectra of the Fe^{57} "probe atoms" were obtained in the usual manner by resonance absorption of the 14.4 keV gamma rays emitted from the "probe atoms" by a Fe^{57} -enriched stainless steel foil. Since the Fe^{57} "probe atoms" originally exist as Co^{57} , the Mössbauer spectra provide information about the chemistry of the cobalt surface. The low scattering cross section of the 14.4 keV gamma radiation permits in situ studies with a reaction cell designed to minimize the amount of solution between the specimen surface and a thin mylar window. A schematic of the experimental arrangement is shown in Fig. 1. The shielding and counter electrode were arranged so that any Co^{57} deposited on this electrode would not interfere with the Mössbauer spectrum originating from the working cobalt electrode. Co^{57} ions present in the solution phase contribute to the count rate, but the ions in solution do not contribute to the Mössbauer spectrum because the recoil-free fraction of nuclei in solution is negligible.

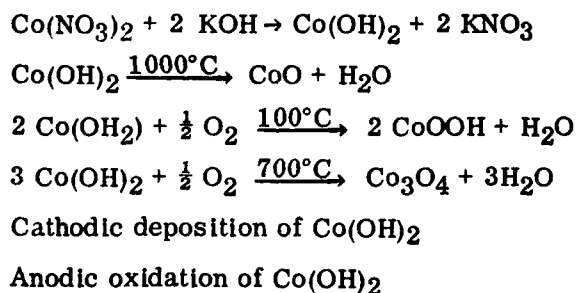
The polarization of cobalt in buffered sodium borate solution at pH 8.5 produces a classical potential vs. current density relationship as shown in Fig. 2. An active-to-passive transition occurs between -500 and -300 mv (vs. SCE) and a passive range exists between -300 and +500 mv where the current density is less than 10^{-6} amp/cm^2 . Above +500 mv the surface film begins to thicken and oxygen evolution occurs. The growth and dissolution rates of the surface films that formed during anodic polarization were determined as a function of time. A typical plot of current density and count rate

as a function of time is shown in Fig. 3 for polarization at +200 mv. At anodic potentials higher than +200 mv the dissolution or corrosion rate was sufficiently slow that emission spectra could be readily obtained before the Co^{57} -active-surface region of the specimen was lost. Studies in the region, -300 to +200 mv, were more difficult because of the rapid loss of surface activity during polarization at these potentials. Experiments at anodic potentials below +200 mv were accomplished by lowering the specimen temperature and removing the applied potential after the passive films were formed.

To characterize the surface chemical species present during polarization, emission Mössbauer spectra were obtained at specific applied cathodic and anodic potentials. Emission spectra of specimens taken during cathodic polarization at -1100 mv, Fig. 4, showed only the six lines expected from the magnetic hyperfine splitting of Fe^{57} in metallic cobalt. This result indicates that atoms at the surface of cobalt are essentially in a zero valence state during cathodic polarization, and that any "oxide" formed during specimen preparation and transfer to the electrolytic cell was readily reduced by the cathodic treatment. Two additional resonance lines of equal intensity were observed in the emission spectra during anodic polarization at +200 mv and +500 mv. An emission spectrum from the passive film taken during polarization at +500 mv is shown in Fig. 5. The unoxidized component has been subtracted from the spectrum in order to resolve better the spectrum of the passivating surface film. These new lines occurred at -1.02 mm/sec and -0.11 mm/sec (vs. stainless steel) for both anodic potentials. The surface film produced at +200 mv and +500 mv, therefore, gives an emission Mössbauer spectrum with an isomer shift of 0.57 mm/sec and a quadrupole splitting of 0.91 mm/sec. The isomer shift is characteristic of Fe^{+3} (i.e., Co^{+3}). For polarization at anodic potentials higher than +500 mv the Mössbauer spectrum indicated the presence of an additional

resonance line near the -0.11 mm/sec peak in the spectra of the passive films formed at +200 and +500 mv. This change in the spectrum is apparently caused by the formation of an Fe^{+4} (i.e., Co^{+4}) valence state at the surface of cobalt during polarization in the transpassive region. Emission spectra obtained at -100 mv indicated the presence of both Fe^{+2} and Fe^{+3} (i.e., Co^{+2} and Co^{+3}) in the passive film.

To interpret the emission spectra obtained during anodic polarization of cobalt, two important considerations must be taken into account: (1) The Auger cascade that follows the electron capture decay conversion of Co^{57} to Fe^{57} may lead to non-equilibrium charge states on the Fe^{57} "probe atom" and (2) the preferred charge state of Fe^{57} in a cobalt compound may be different than the charge state of the parent Co^{57} . In view of the possibility that the charge on the Fe^{57} "probe atoms" may not represent the charge on the Co^{57} parent, emission spectra were obtained from the cobalt oxides, hydroxides and oxyhydroxides to serve as a basis for interpreting spectra from the passivated surfaces. The Co^{57} -doped cobalt compounds were prepared according to the following reactions:



The Mössbauer parameters obtained from each of the cobalt compounds and from the cobalt surface polarized at +200 and +500 mv are summarized in Table I.

The parameters derived from emission spectra of the passive films formed at +200 and +500 mv are in closest agreement with the parameters obtained from the spectrum of anodically oxidized hydroxide. A spectrum of the CoOOH formed by anodic oxidation of $\text{Co}(\text{OH})_2$ at pH 8.5 and +500 mv is shown in Fig. 6. These results suggest that the

principal component of the passive film formed at these potentials is a hydrated cobaltic hydroxide. The emission spectrum obtained at -100 mv was similar to the emission spectrum from blue $\text{Co}(\text{OH})_2$. A Fe^{+3} component was observed in the spectra from both of the reference (blue) hydroxides prepared either by precipitation or cathodic deposition as well as in the passive film formed at -100 mv. It is not clear from our data whether the Fe^{+3} component in this compound and in the passive film originates from the aftereffects following the Auger cascade or from partial oxidation.

It is apparent from the results of these Mössbauer studies of the anodic behavior of cobalt that (1) $\text{Co}(\text{OH})_2$ is formed at the surface for anodic potentials between -300 mv and +200 mv, (2) a hydrated cobaltic hydroxide, CoOOH , is formed at potentials above +200 mv, and (3) the outer surface is further oxidized to a (+4) valence state in the transpassive potential region above +500 mv.

TABLE I

Mössbauer Parameters for Co-57 Doped Cobalt Compounds

Compound	Preparation Method	Type of Computer Fit	Temp.	Doublet		Singlet Isomer Shift mm./sec.
				Isomer Shift mm./sec.	Quadrupole Splitting mm./sec.	
CoO	Heated $\text{Co}(\text{OH})_2$ at 1000°	Singlet	25°	-----	----	-1.159
Co_3O_4	Heated $\text{Co}(\text{OH})_2$ at 400°	Doublet and Singlet with Variable Linewidth	25°	$-0.403 \pm .003$	$0.602 \pm .020$	$-0.377 \pm .002$
			-196°	$-0.561 \pm .002$	$0.732 \pm .006$	$-0.525 \pm .001$
Blue $\text{Co}(\text{OH})_2$	(1) Pptn. from NO_3 soln.	Two Doublets	25°	$-1.296 \pm .007$	$2.460 \pm .015$	-----
	(2) Cathodic deposition from NO_3 soln.		-196°	$-0.538 \pm .012$	$0.829 \pm .029$	-----
Pink $\text{Co}(\text{OH})_2$	Pptn. from nitrate soln.	Two Doublets	25°	$-1.389 \pm .006$	$2.737 \pm .013$	-----
			-196°	$-0.581 \pm .015$	$1.049 \pm .029$	-----
CoOOH	Air oxidation of $\text{Co}(\text{OH})_2$ in alkaline soln.	One Doublet	25°	$-1.392 \pm .003$	$2.759 \pm .006$	-----
			-196°	$-0.293 \pm .008$	$1.184 \pm .015$	-----
Blue $\text{Co}(\text{OH})_2$ Anodically Oxidized at +500 mv.	At pH 8.5	One Doublet	25°	$-1.428 \pm .004$	$3.074 \pm .007$	-----
			-196°	$-0.572 \pm .015$	$0.797 \pm .025$	-----
Passive Film at +200 mv.	In borate soln.	One Doublet	25°	$-0.413 \pm .006$	$1.067 \pm .035$	-----
			-196°	$-0.550 \pm .004$	$1.141 \pm .023$	-----
Passive Film at +500 mv.	In borate soln.	One Doublet	25°	$-0.562 \pm .006$	$0.805 \pm .010$	-----
			-196°	$-0.547 \pm .008$	$0.939 \pm .013$	-----

Figure Captions

- Figure 1. Schematic diagram of reaction cell used in obtaining in situ Mössbauer spectra of the passive film on cobalt.
- Figure 2. Polarization curve for cobalt in a solution containing 0.15 N sodium borate and 0.15 N boric acid at pH 8.5.
- Figure 3. Current density and radioactivity of cobalt surface as a function of time when sample was polarized at +200 mv vs. S. C. E. in the borate solution at pH 8.5.
- Figure 4. Mössbauer emission spectrum of a 50 Å film of electrodeposited cobalt doped with Co^{57} while cathodically treated at -1100 mv in a borate buffer at pH 8.5.
- Figure 5. Mössbauer emission spectrum of the passive film on cobalt while under anodic treatment in borate buffer at pH 8.5 at +500 mv. Spectrum is the computer fit after subtraction of the spectrum of unreacted elemental cobalt.
- Figure 6. Mössbauer emission spectrum from $\text{Co}(\text{OH})_2$ deposited on platinum electrode and anodized at +500 mv. Compare with Figure 5.

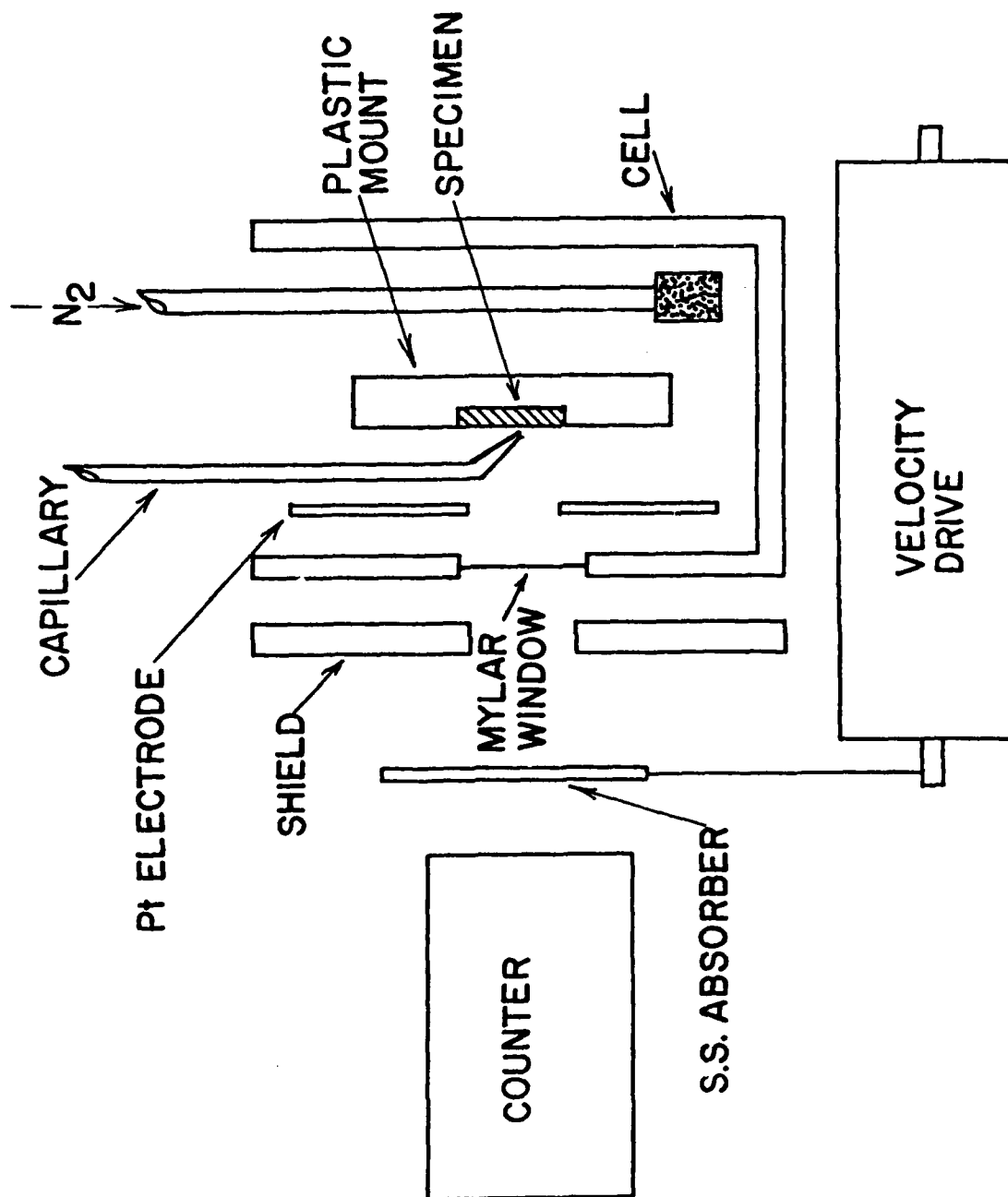


Figure 1

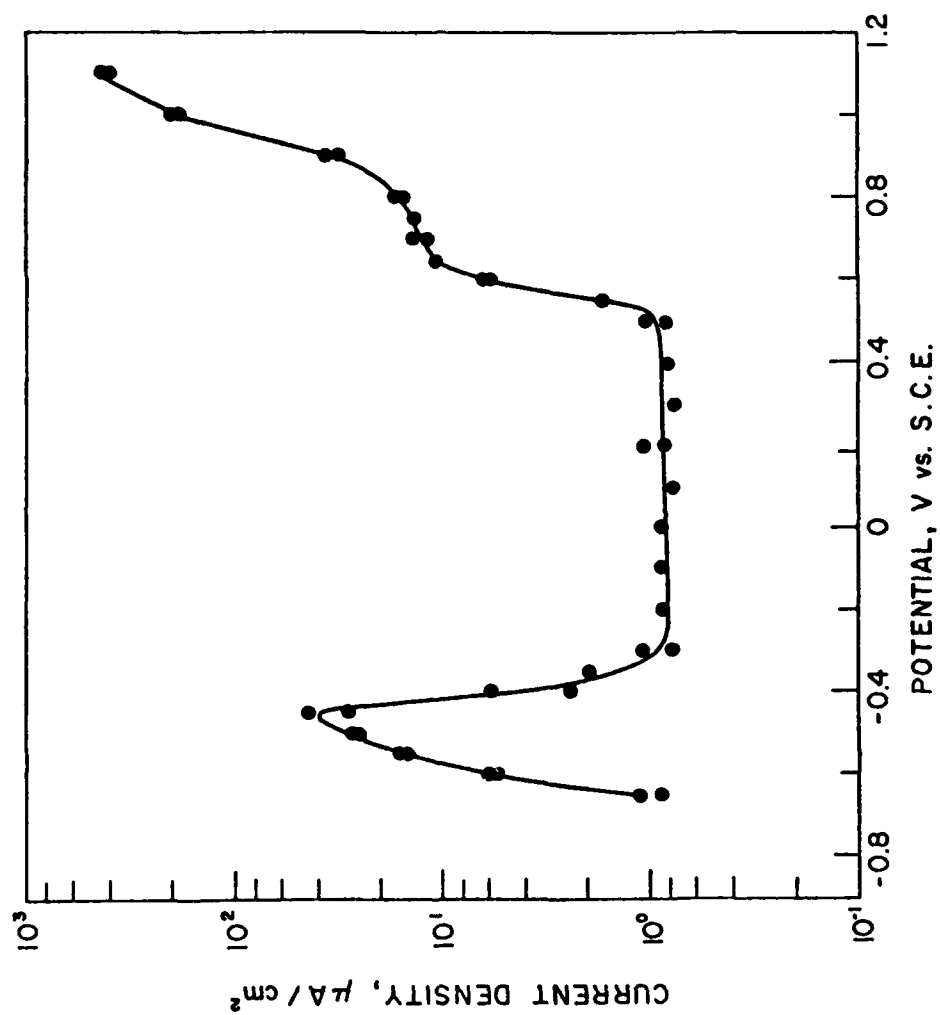


Figure 2

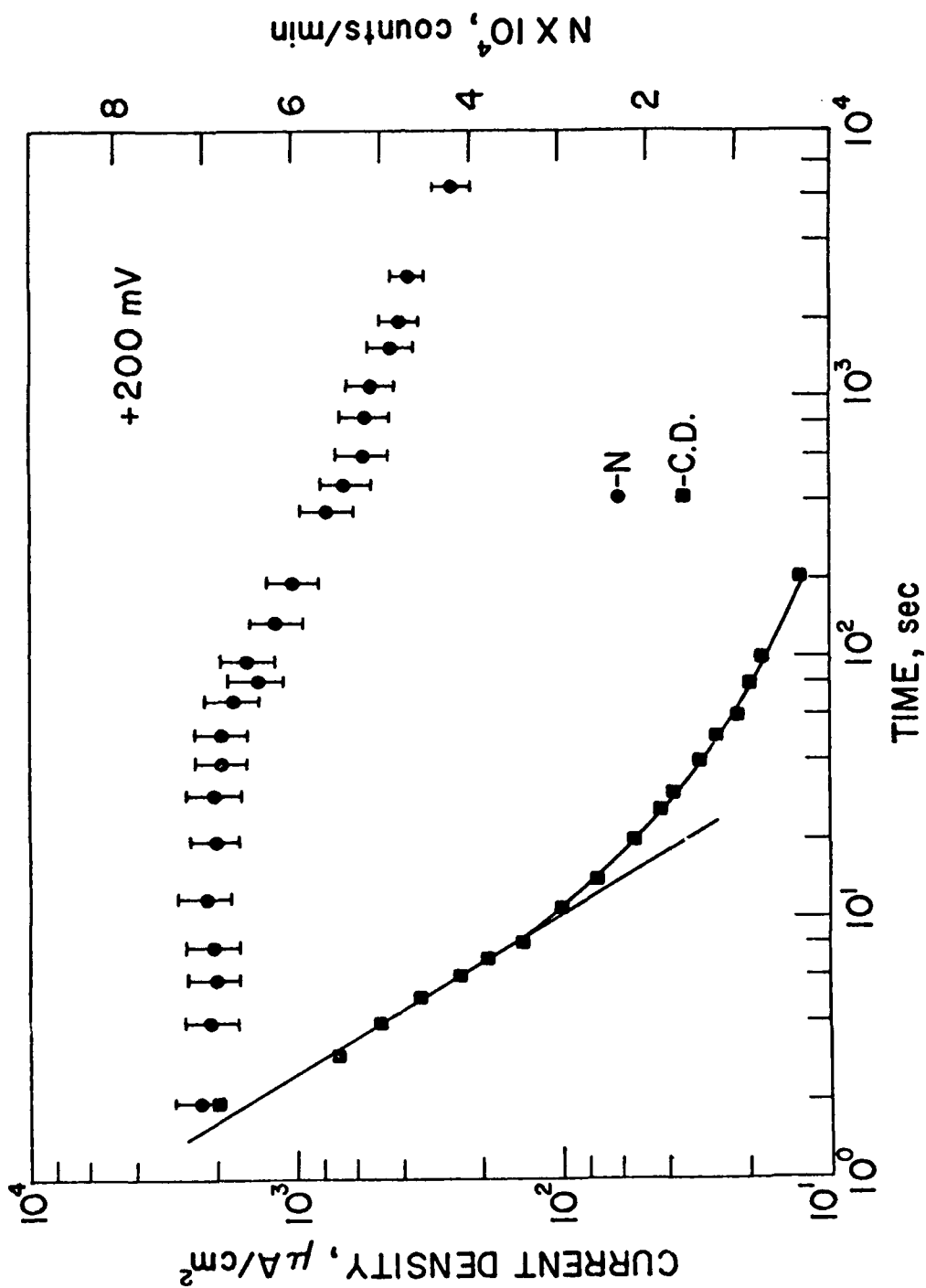


Figure 3

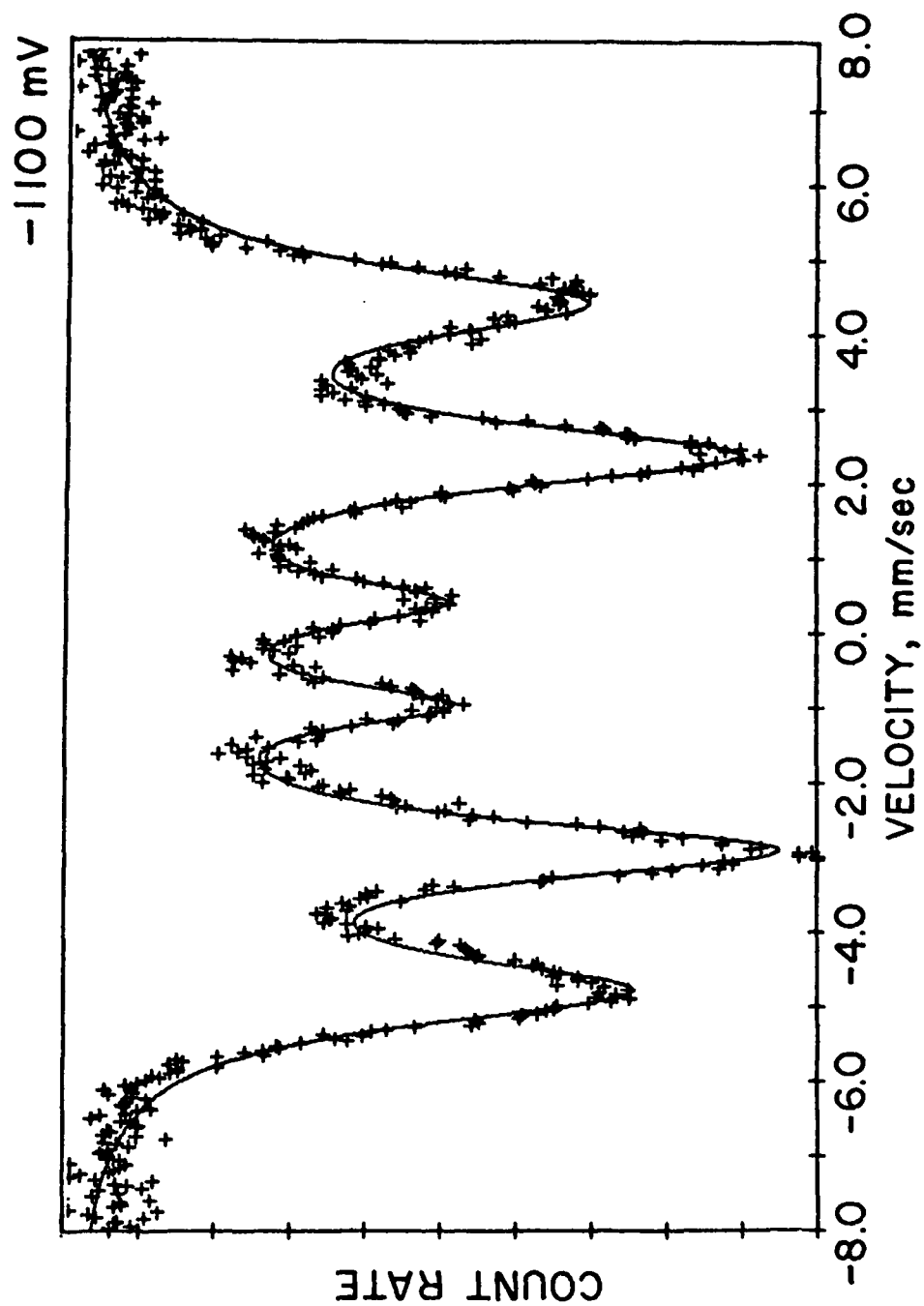


Figure 4

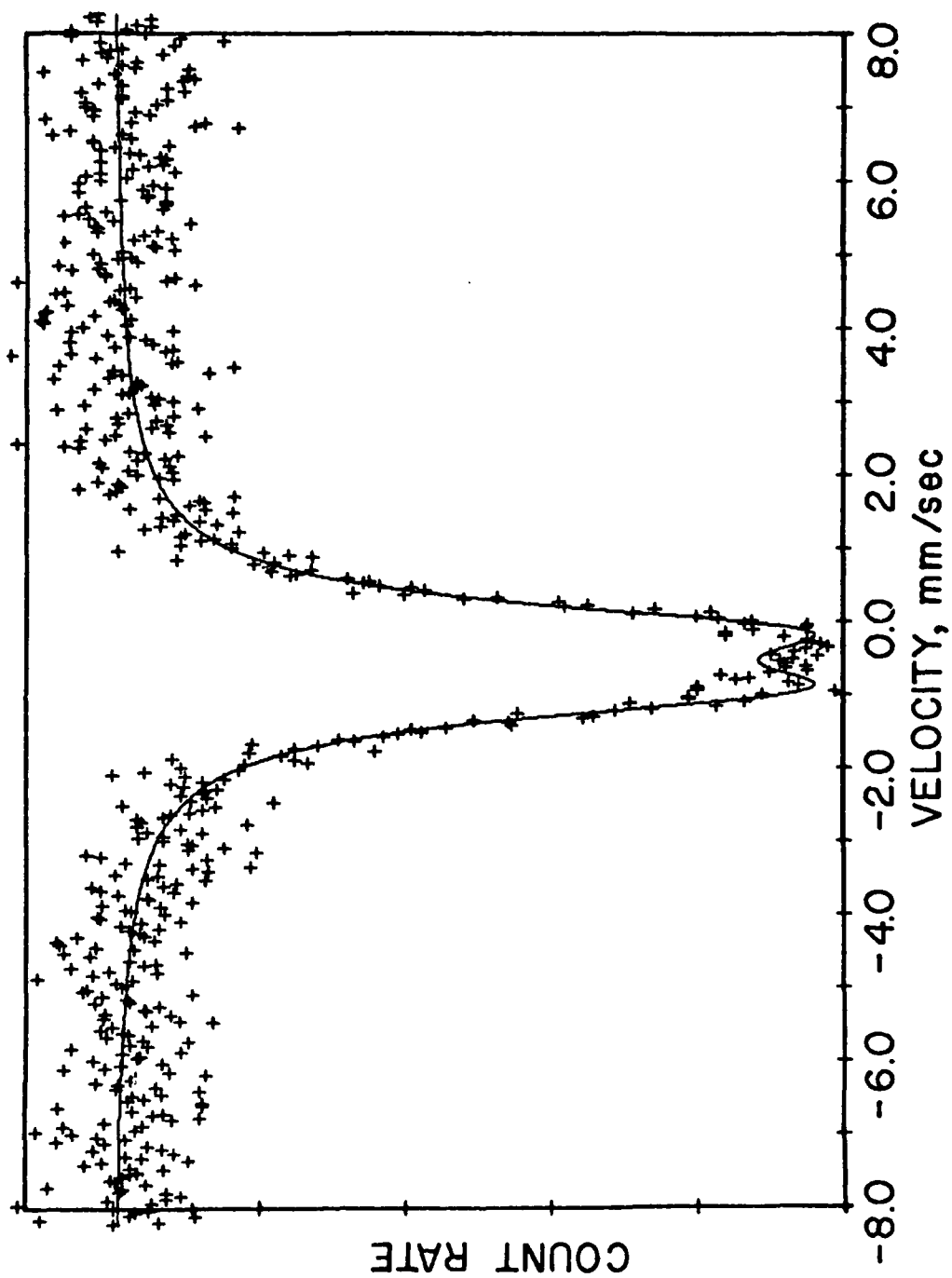


Figure 5

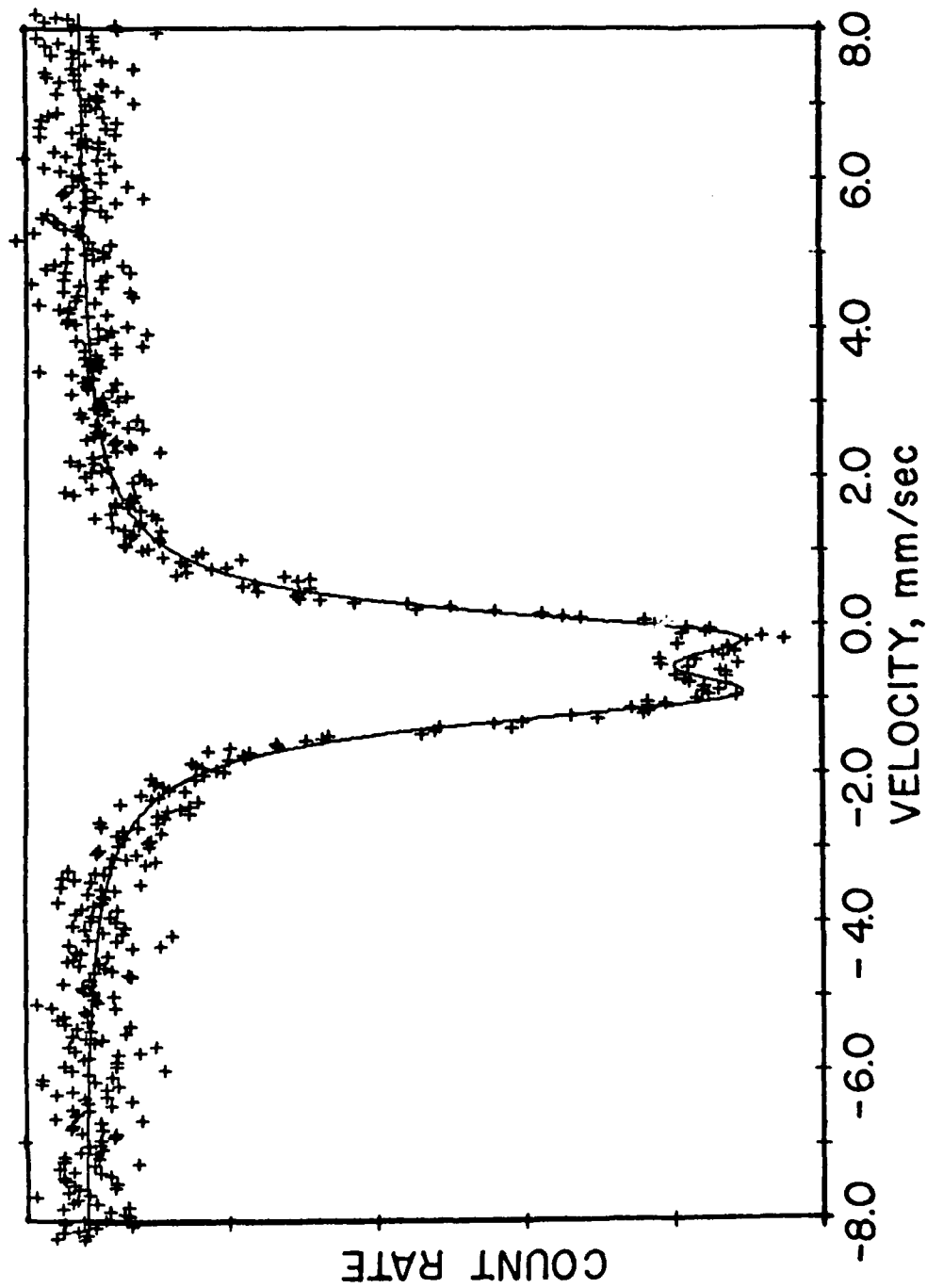


Figure 6